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# CATALYTIC AGENT DEGRADATION ON OXIDE FILMS AND IN MICROHETEROGENEOUS SOLUTION SYSTEMS

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**Fourth Interim Report**

by

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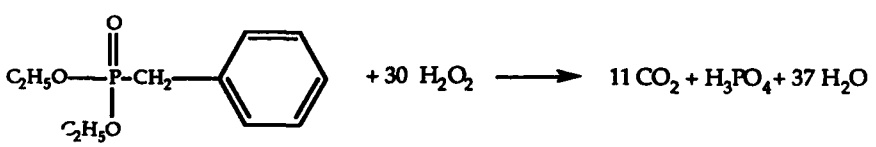
The investigation over the last six month period of contract no. DAJA45-90-C-0007 concerns the mineralization of organophosphonates in aqueous solutions in the presence of Fe (III) peroxides. A striking enhancement by visible light of the peroxidase activity of the reactive intermediate formed under these conditions is reported. Experiments centered principally on the degradation of the compound diethyl-benzylphosponate.

Experiments employed 20 ml aqueous solutions of $5 \times 10^{-3}$ M diethyl-benzylphosphonate contained in 130 ml glass vials closed with a septum and immersed in a thermostated water bath. The time course of the mineralization of the phosphonate was followed by withdrawal of samples of liquid and gas and analyzing the total organic carbon (TOC) and $CO_2$ content, respectively. The TOC analysis was carried out with a Shimatsu instrument, while carbon dioxide was analyzed by gas chromatography using a Poropack column and helium as the carrier gas.

Fig. 1 shows the decline of the percentage of TOC present in the solution as well as the increase in the amount of $CO_2$ generated as a function of reaction time. The solutions contained $10^{-2}$ M $Fe(NO_3)_3$ and 0.3 M $H_2O_2$ in addition to $5 \times 10^{-3}$ M DBP. In the beginning, the pH of the DBP solution was 5.9, decreasing to 2.25 after $Fe(NO_3)_3$ addition. $H_2O_2$ addition initially caused a further decrease of the pH to 1.6 followed by an increase in the pH to a value of 1.75 after complete mineralization of the DBP. The $CO_2$ is expressed in units of percentage conversion with respect to the stoichiometry of eq. 1, which describes complete mineralization of the organo-phosphonate:

<u>Equation 1</u>:




In the dark at 50°C, the TOC value declines within ca. one hour to a plateau value corresponding to 40-50% of its initial value. The TOC decrease is accompanied by the generation of $CO_2$ confirming the occurrence of the total oxidation of the organophosphonate. This initial phase is followed by a much slower decomposition of the DBP. Illumination by visible light ($\lambda >$ 435 nm) sharply accelerates destruction of the organophosphonate. Bubbles of $CO_2$ are vigorously evolved from the solution under irradiation. After 20 min. reaction time, ca. 90% mineralization is achieved. Further addition of 67 micromoles of $H_2O_2$ at this point and continued exposure to visible light for another 20 min. led to the complete destruction of the organophosphonate. The organic carbon content of the solution decreased below detection limit (1ppm), and ca. 27 ml (STP) of $CO_2$ was generated in agreement with the stoichiometry of reaction (1).

A blank experiment was carried out in the absence of Fe(III) at 50°C under otherwise identical conditions as employed in **Fig. 1**. Practically no mineralization of DBP was observed even under light excitation confirming the key role of Fe(III) in the phosphonate decomposition process.

The effect of visible light is even more striking when the Fe(III) catalyzed mineralization of the organophosphonate is performed at room temperature. In the experiment depicted in **Fig. 2**, 4 vials with the same initial content of $Fe(NO_3)_3$, $H_2O_2$ and DBP were run in parallel. These samples were subjected to visible light illumination after various dark reaction times. In the dark, $CO_2$ evolution according to **eq. (1)** is again biphasic. The rate of the fast part is about 10 times lower than that observed at 50°C, the plateau corresponding to 40% conversion being attained after 10 hours. During the subsequent phase, $CO_2$ evolution is slow, the conversion of the DPB proceeding only a few percentage points after 30 additional hours. However, during this slow mineralization process, visible light excitation always led to a striking enhancement of the mineralization rate of the organophosphonate as shown by the dashed lines. Even for the sample that was kept in the dark for 40 hours, the $CO_2$ pressure rises practically vertically on the time scale of **Fig. 2**, rapidly approaching the stoichiometric limit. This visible light enhancement is so pronounced that it is readily detectable even in the presence of the very weak photon flux generated by neon lamp room light. These experiments indicate that there is a long-lived intermediate formed in aqueous DBP solutions in the presence of peroxide and Fe(III) whose oxidizing activity with respect to the organophosphonate is sharply increased by visible light excitation.

Direct evidence for the formation of this intermediate was obtained by optical absorption spectroscopy. Upon addition of $H_2O_2$ to solutions containing DBP and $Fe(NO_3)_3$, the solution turns intensely black brown. The color fades rapidly within a few minutes to yield a brownish yellow colored species. The difference spectrum obtained 2 minutes after mixing [ref. solution DBP and $Fe(NO_3)_3$] has a maximum at 380 nm and a tail extending through the entire visible region until 800 nm with a shoulder around 550 nm. The long wavelength tail of this spectrum decays within only a few minutes, while at shorter wavelengths the decrease is greatly diminished. In the dark at 50°C, about half of the 380 nm absorbance decays within 30 to 60 minutes, the other half being long-lived. Under visible ($\lambda >$ 435 nm) light illumination, the 380 nm absorbance disappears very rapidly and completely within less than 10 min.

These spectroscopic findings indicate that there are at least two intermediates involved in the mineralization of the organophosphonate. The organophosphonate complexes Fe(III) via the oxygen of the P=O groups, which are known to be excellent $\sigma$ donors. Upon addition of $H_2O_2$, a highly colored peroxo complex is formed. As in the case of the violet $H_2O_2$ adduct of Fe(III)EDTA, the intense visible transition is probably a $HOO^- \rightarrow$ Fe(III) charge transfer band. In the next step $OH^-$ is lost from the complex resulting in the formation of a ferryl species where the formal oxidation state of iron

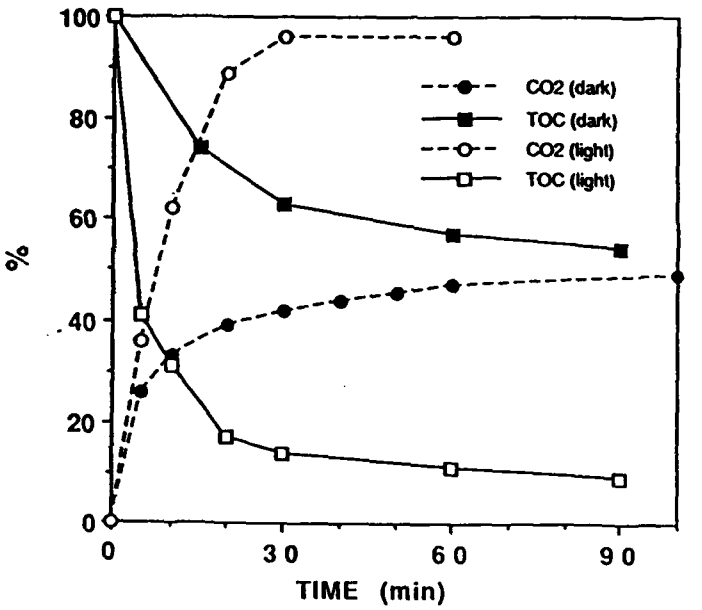
is five. The yellow-brown colored intermediate with $\lambda_{max}$ at 380 nm is tentatively identified as a high-valency iron complex with DBP. The high potential of Fe in such a complex induces its autodestruction via oxidation of the ligand to $CO_2$ and release of inorganic phosphate. For reasons which need to be explored, this reaction is biphasic in the dark, the faster and slower part contributing about equally to the decomposition. Undoubtedly, the activity of this intermediate Fe species is strongly enhanced by visible light resulting in the greatly accelerated and complete mineralization of the DBP ligand.

The outcome of these experiments under various conditions were analyzed as depicted in **Figs. 3-7**. **Fig. 3** illustrates the influence of the amount of $H_2O_2$ and the mode of addition on the completion of the degradation reaction of DBP. Thus, three subsequent additions of 0.6 equivalents of $H_2O_2$ resulted in the same ultimate yield of $CO_2$ as two equivalents added initially. The catalytic destruction of $H_2O_2$ by $Fe(NO_3)_3$ is at least partially circumvented. The ratio of DBP : $Fe(NO_3)_3$ likewise plays a decisive role in the quantitative decomposition of this organophosphonate (**Fig. 4**), the ratio 1 : 3 exhibiting optimal $CO_2$ evolution. The nitrate, sulfate, chloride and perchlorate ferric salts were all tested for their efficiency as catalysts, $Fe(NO_3)_3$ being the most effective (**Fig. 5**).

Comparative studies with other catalysts such as $Cu(NO_3)_2$ or $TiO_2$ in conjunction with $H_2O_2$ (**Figs. 6 and 7**) uphold the exceptional enhancement of both the thermal and light-induced catalytic degradation of the organophosphonate, DBP, by peroxoiron (III) complexes.

**FIG. 1**

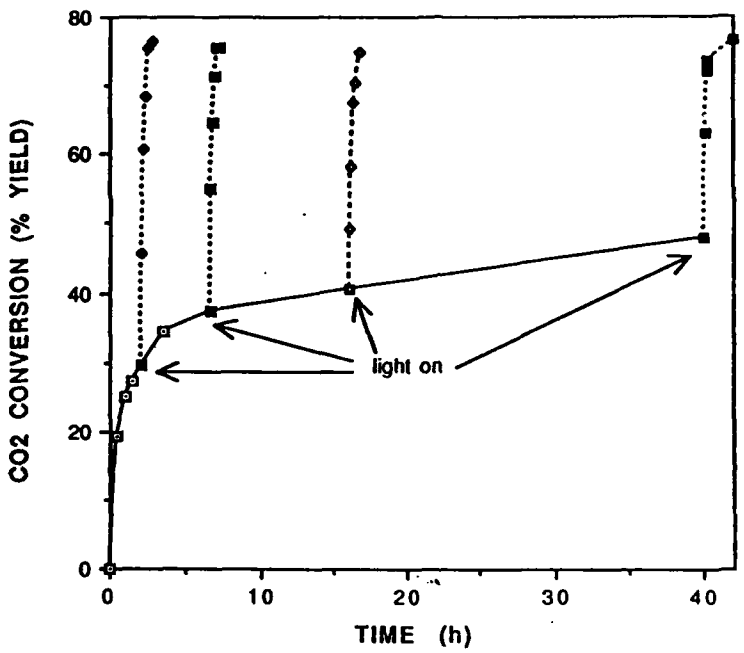
**$CO_2$ production and decline in total organic carbon (TOC) during the Fe(III) catalyzed mineralization of diethylbenzyphosphonate (DBP)**




Conditions: 0.3M $H_2O_2$, 0.01M $Fe(NO_3)_3$, 0.005M DBP,T = 50°C

FIG. 2

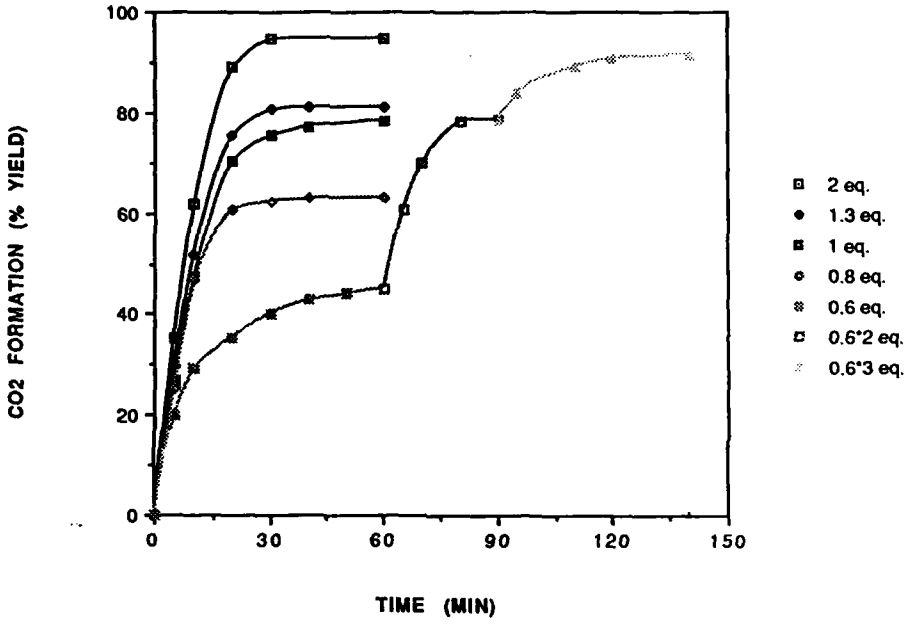
**$CO_2$ generation from the Fe(III) catalyzed mineralization of DBP**




4 vials each containing 20 ml solution:
0.3M $H_2O_2$, 0.01M $Fe(NO_3)_3$, 0.005M DBP, T = 25°C

FIG. 3

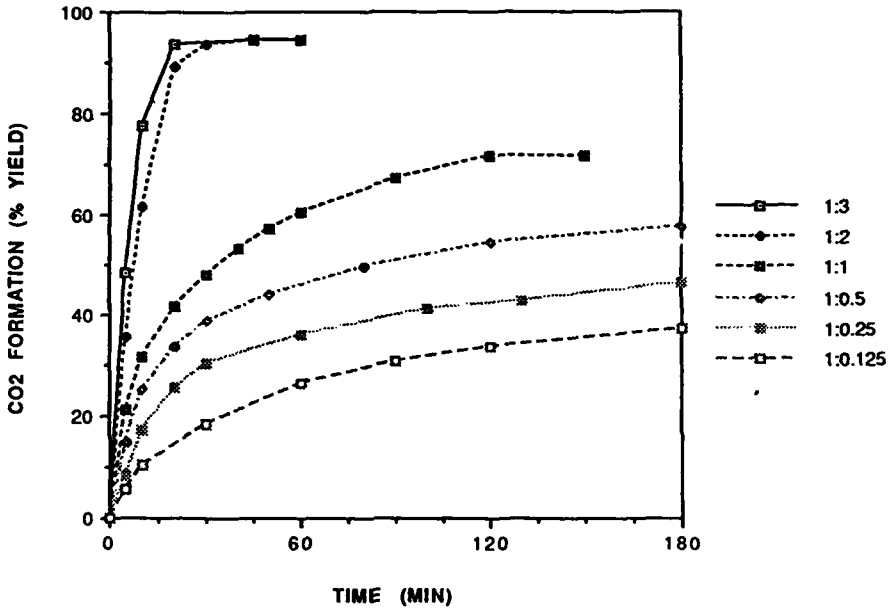
**Effect of Sequential Addition of $H_2O_2$ on Phosphonate (DBP) Degradation**




$H_2O_2$ 0.3M, DBP $5.10^{-3}$M,
DBP: $Fe(NO_3)_3$ = 1:2
hv>435 nm T = 50°C

FIG. 4

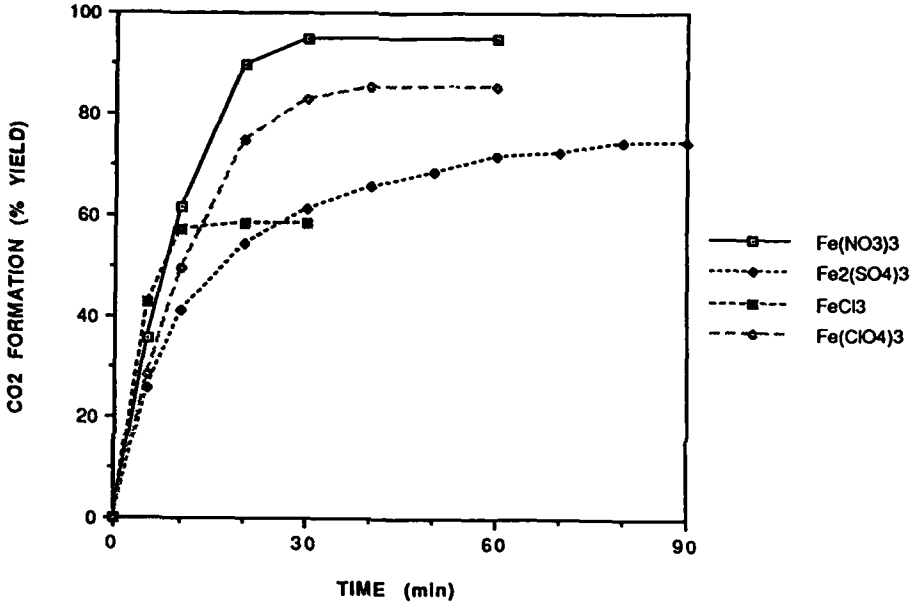
**Photodegradation of Diethylbenzylphosphonate (DBP) by Fe(III) Peroxides Influence of DBP: $Fe(NO_3)_3$ Ratio**




DBP = $5.10^{-3}$M, $H_2O_2$ = 2 equivalents
hv > 435, T = 50°C

FIG. 5

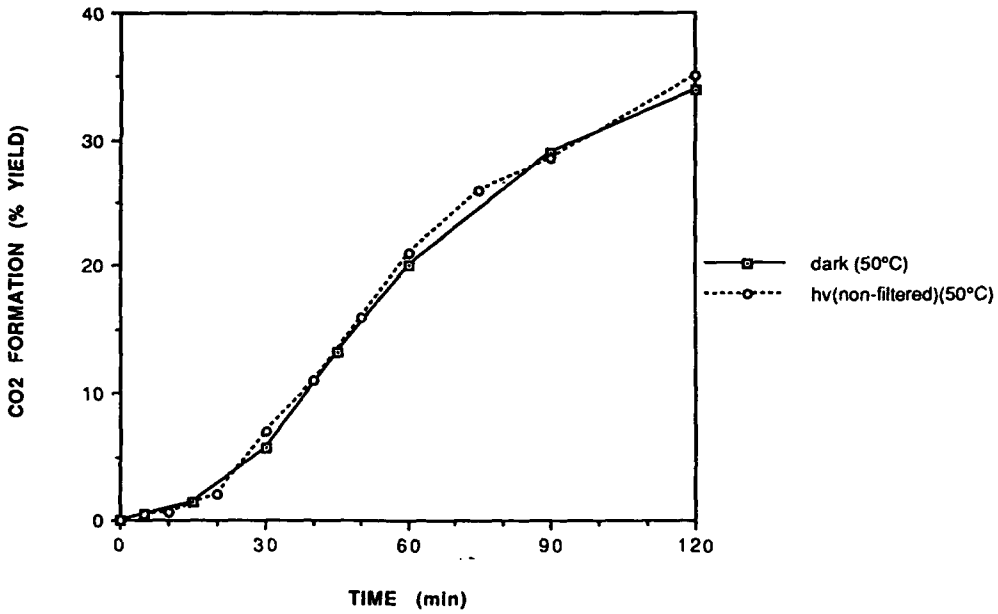
**Photodecomposition of Diethylbenzylphosphonate (DBP) in Presence of Various Iron Salts**




DBP = $5.10^{-3}$M, $H_2O_2$ = 2 eq., DBP : Fe(III) = 1:2,
hv > 435 nm, T = 50°C

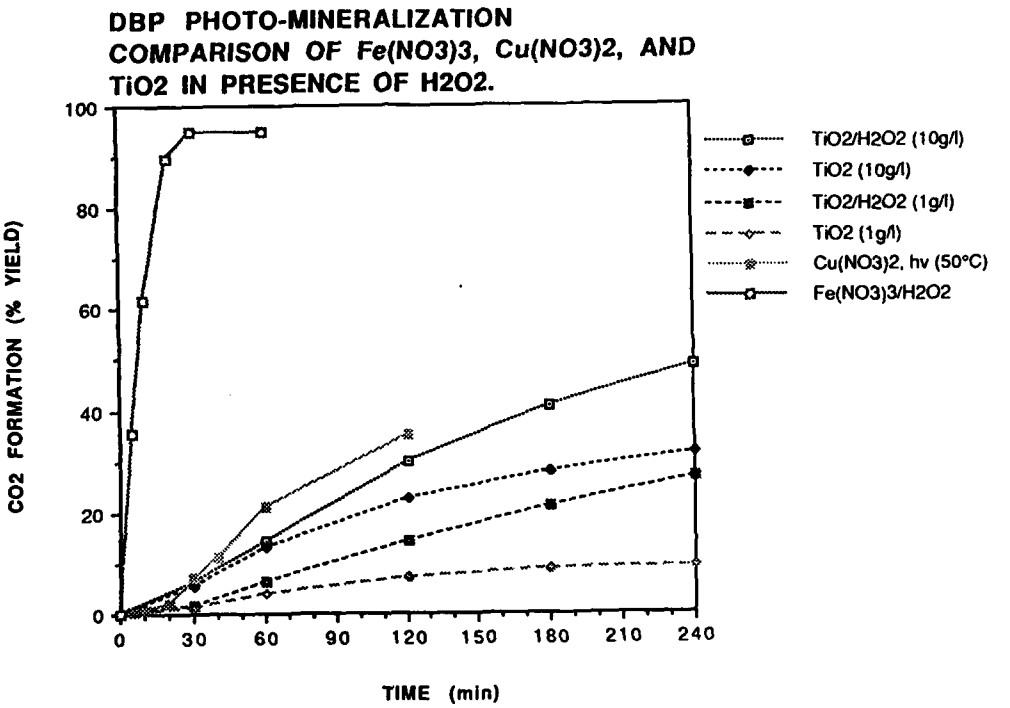
FIG. 6

**DBP DECOMPOSITION IN PRESENCE OF Cu(NO3)2 and H2O2**




DBP = $5 \cdot 10^{-3}$M, $Cu(NO_3)_2$ = $1 \cdot 10^{-2}$M,
$H_2O_2$ = 0.3M

FIG. 7




DBP = $5 \cdot 10^{-3}$M, $Fe(NO_3)_3 = Cu(NO_3)_3 = 1 \cdot 10^{2}$M,
$H_2O_2$ = 0.3M